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TECHNICAL MEMORANDUM 1235

INVESTIGATION OF CONDITIONS OF TITANIUM CARBONIZATION - IV

By G. A. Meerson and Y. M. Lipkes

Translation

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INVESTIGATION OF CONDITIONS OF TITANIUM CARBONIZATION - IV

By G. A. Meerson and Y. M. Lipkes

In a previous paper (reference 1), results are presented of accurate investigations of the processes of titanium carbonization and the succeeding titanium carbide decarbonization as related to the phenomenon of the graphitization of soot by heating at a constant temperature in atmospheres of pure hydrogen and carbon monoxide. These tests showed that the processes of titanium carbonization-decarbonization in an atmosphere of pure gases without nitrogen proceed in the same direction as the analogous processes (references 1 and 2) under the conditions of the production furnace. In this case, however, the presence of admixtures of nitrogen changes the quantitative results of the decarbonization process.

Thermodynamic computations confirming the results of previous tests conducted at atmospheric pressure and additional tests of titanium carbonization at lowered pressures are presented herein.

EVALUATION OF TEST RESULTS ON PROCESS OF TITANIUM

CARBONIZATION AT ATMOSPHERIC PRESSURE

Thermodynamic Computations

The purpose of the following computations is to confirm that the order of experimentally determined magnitude of the lowering in content of the combined carbon by exposing titanium carbide at constant temperature can be based on energy changes occurring in the system as a result of graphitization of initial soot (used for titanium carbonization).

(1) Carbonization in an atmosphere of carbon monoxide. By considering the reaction



*"Issledovania Uslovii Carbonizatsii Tetana." Zhournal Prikladnoi Khimii. Vol. 18, nos. 4-5, 1945, p. 251-258.

and by assuming the formation of a continuous series of solid solutions of TiO - TiC, the equilibrium constant for reaction (1) is formed as

$$K = P_{\text{CO}} \frac{[\text{TiC}]}{[\text{TiO}]} \quad (2)$$

where $\frac{[\text{TiC}]}{[\text{TiO}]}$ is equal to the ratio of the molar concentrations of TiC to TiO in the solid solution with the products of carbonization.

The assumption of the continuous series of solid solutions TiO - TiC is based on the fact that TiO and TiC crystallize in the same type of lattices with close periods (4.15 Å and 4.32 Å, respectively). This assumption is, by X-ray investigations of different points of the system TiO - TiC, unconditionally confirmed in the range of states above 10 percent C_{comb} and does not contradict it even in the range of small carbon content; however, in this range, the number of investigated points for establishing the continuity of the series TiO - TiC over the entire range is insufficient.

It is necessary, moreover, to consider that the behavior of the system TiO - TiC may differ from the behavior of the usual solid solutions because in passing from TiO to TiC, the character of the interatomic bonds in the lattice is changed (from prevailing ionic bonds to prevailing metallic bonds). Thus, the mathematical laws following from equation (2) may not be observed over the entire range of the series TiO - TiC.

In the computed results given herein as compared with the experimental results, however, the system TiO - TiC is considered only in a certain limited range where the existence of solid solutions is known.

For these tests, $P_{\text{CO}} = 1$ atmosphere and $K = \frac{[\text{TiC}]}{[\text{TiO}]}$.

For reaction (1) with graphite, the dependence of the equilibrium constant on the temperature is expressed by

$$\lg K'_p = \lg \frac{[\text{TiC}]}{[\text{TiO}]} = - \frac{\Delta F^\circ}{4.571 \cdot T} \quad (3)$$

where ΔF° is the free energy of the carbonization reaction (1).

For the same reaction with soot ("atmospheric" coal)

$$\lg K_p'' = \lg \frac{[T1C]''}{[T1O]''} = - \frac{[\Delta F^\circ - 2\Delta f^\circ]}{4.571 \cdot T} \quad (4)$$

where Δf° is the free energy of the graphitization of coal.

By subtracting equation (3) from equation (4), the following equation is obtained for 1900° C (production temperature of carbonization):

$$\lg K_p'' - \lg K_p' = \lg \frac{[T1C]''}{[T1O]''} - \lg \frac{[T1C]'}{[T1O]'} = \frac{2\Delta f^\circ}{4.571 \cdot 2173} \quad (5)$$

For the approximate computation of the magnitude of free energy of graphitization Δf° , Falke's equations (reference 3) are used by giving the values of the equilibrium constants of the Budoir reaction for the cases with graphite and with atmospheric carbon and by extrapolating these equations to 1900° C.

By computing the values of $\lg K_p$ for the Budoir reaction, $C + CO_2 = 2CO$, for the cases with graphite and atmospheric carbon, the corresponding values of the free energy are derived, starting from the relations

$$- \Delta F^\circ_{\text{graphite}} = - \lg K_{p,\text{graphite}} \cdot 4.571 \cdot T$$

$$- \Delta F^\circ_{\text{amorphous}} = - \lg K_{p,\text{amorphous}} \cdot 4.571 \cdot T$$

The difference between these two values of the free energy of the Budoir reaction corresponds to the free energy of graphitization:

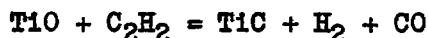
$$\begin{aligned} - \Delta f^\circ &= - [\Delta F^\circ_{\text{graphite}} - \Delta F^\circ_{\text{amorphous}}] \\ &= - 4.571 \cdot 2173 (\lg K_{p,\text{graphite}} - \lg K_{p,\text{amorphous}}) \\ &= - 9165 \text{ calories} \end{aligned}$$

By substituting the value of $-\Delta f^\circ$ as derived from equation (5), the change in state of the titanium-containing phase in equilibrium with either the soot (in the initial period of the carbonization process) or the graphite (after separation of the greater part of the active soot and graphitization of its remainder in the carbonization process) may be computed.

If as initial magnitude the value of $\frac{[TiC]}{[TiO]}$ is taken corresponding to the solid phase of titanium in the stable conditions, that is, after the establishing of equilibrium as a result of prolonged exposure in the furnace, it is then possible to compute the state of titanium carbide at the start of the carbonization process from equation (5).

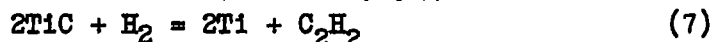
After prolonged exposure, the content of the combined carbon in titanium carbide is assumed to be equal to 17 percent (corresponding to more accurate tests of the present investigation in an atmosphere of pure nonnitrogenous carbon monoxide) and in the presence of "amorphous" carbon (soot), the equilibrium content C_{comb} in the titanium carbide is found to increase up to the level of the theoretical content (computations give 19.9 percent as compared with 20 percent theoretical), which closely agrees with obtained test results where the content of C_{comb} in the presence of soot in the initial stage of carbonization reached 19.2 to 19.6 percent.

(2) Carbonization in an atmosphere of hydrogen. The equation of the total reaction of titanium carbonization in an atmosphere of hydrogen saturated with hydrocarbons is of the same type as the equation of the reaction in an atmosphere of CO



According to reaction (1), the process of titanium decarbonization in an atmosphere of hydrogen will not, however, proceed in the reverse direction as in an atmosphere of carbon monoxide.

According to the reaction, however,



with the corresponding liberation of free carbon



As was previously found, free titanium will not separate out but remains in the same lattice of the type TiC with part "empty" carbon places, which may be considered as a lattice of a solid solution of the pseudobinary system TiC - Ti.

According to the investigations of Y. Umansky and S. Khidekel, the minimum content of combined carbon in the system Ti - C, for which a lattice of the type TiC is maintained, is 7 percent.

By adding reaction (7) with the simultaneously proceeding reaction (8) of the carbon with the hydrogen, the following total reaction is obtained:



By analogous considerations, the equilibrium constant of reaction (9) can be formed as a function of the variable state of the solid titanium phase by accounting for the restriction of the solid solution TiC - Ti

$$K = \frac{\frac{[\text{TiC}]_{\text{true}}}{[\text{TiC}]_{\text{saturated}}}}{\frac{[\text{Ti}]_{\text{true}}}{[\text{Ti}]_{\text{saturated}}}}$$

or

$$K = a \frac{[\text{TiC}]}{[\text{Ti}]}$$

where a is a constant factor related to the concentration of the saturated solid solution of Ti in TiC.

By comparing the conditions of equilibrium of reaction (9) in the presence of "amorphous" carbon at the start of the carbonization process and in the presence of graphite after a prolonged exposure, the following equation is obtained analogous to equation (5) of the preceding section:

$$\lg K'' - \lg K' = \left[\lg \frac{[\text{T1C}]''}{[\text{T1}]''} + \lg a \right] - \left[\lg \frac{[\text{T1C}]'}{[\text{T1}]'} + \lg a \right]$$

or for 1900° C

$$\lg K'' - \lg K' = \lg \frac{[\text{T1C}]''}{[\text{T1}]''} - \lg \frac{[\text{T1C}]'}{[\text{T1}]'} = \frac{2\Delta f^\circ}{4.571 \cdot 2173} \quad (10)$$

where Δf° is the free energy of graphitization, 9165 calories.

Thus for the given case, the change in state of the titanium phase in equilibrium either with the soot or with the graphite may be as readily computed as for the system



and these computations lead to the same results as the analogous computations for the system $\text{T1O} - \text{T1C}$, namely, that in the presence of soot under metastable conditions at the start of the carbonization process, a content of C_{comb} that is near the theoretical value may be obtained in the titanium carbide.

Experimental data likewise show that the content of combined carbon in titanium carbide, both for the stable conditions after prolonged exposure as well as for the metastable conditions of the initial period of exposure, agree for the cases where the reactions proceed in an atmosphere of pure CO and of pure H_2 .

It would appear that the reaction $\text{T1O} + 2\text{C} = \text{T1C} + \text{CO}$, accounting for the formation of the solid solution $\text{T1O} - \text{T1C}$ from blowing hydrogen through the furnace and washing out the CO from the reaction chamber, should proceed from left to right.

The fact that heating a mixture of carbon monoxide with carbon results in a continuous separation of carbon monoxide from the surface of the particles $\text{T1O} - \text{T1C}$ must be considered. Under these conditions, it may be assumed that on the surface of the particles $\text{T1O} - \text{T1C}$ a certain adsorption layer of the carbon monoxide is maintained; thus independently of the dilution of carbon monoxide by the surrounding hydrogen, the newly formed molecules of CO must overcome the total pressure of the surrounding gas medium and not the pressure corresponding to the lowered partial pressure of the CO.

Shenk arrived at a similar conclusion with regard to the direct formation of iron (reference 4).

The preceding considerations concerning the mechanism of titanium carbonization and decarbonization in an atmosphere of CO and H₂ and the change in state of the solid phase as a function of the change in concentration of the hydrocarbons in the gas medium may be represented by the hypothetical trinary diagram (fig. 1).

The system Ti - TiC in figure 1 differs from the system TiO - TiC in that in the first case there is a boundary of the region of solid solutions Ti - TiC with a 7 to 20 percent range in carbon content. Below 7 percent of C_{comb}, there is a new solid phase that, under the conditions of a hydrogen medium, may be represented as a phase based upon titanium hydride.

DEPENDENCE OF STATES OF TITANIUM-CARBONIZATION PRODUCTS ON PRESSURE AND TEMPERATURE

The investigations described have shown that within the range of temperatures up to 2000° C at atmospheric pressure it is impossible to obtain pure titanium carbide of theoretical composition under stable conditions. The shifting of the equilibrium of the reaction $TiO + 2C = TiC + CO$ from left to right is possible by decreasing the pressure in the reaction space.

The following tests concern titanium carbonization at lowered pressures. These tests were conducted in the same electrical furnace previously described in reference 2 in an atmosphere of pure carbon monoxide. For the maximum approach to the conditions of equilibrium, an attempt was made to obtain a constant composition of the carbonization product for each test by doubling the exposure time. After the required exposure and the cooling of the furnace, a sample was taken for analysis.

The conditions of the tests and their results are shown in table I and in figures 2 and 3.

CONCLUSIONS

1. The study of the process of titanium carbonization at 1900° C by heating a mixture of $TiO_2 + C$ in atmospheres of pure

carbon monoxide and pure hydrogen confirmed previous observations (conducted under production-furnace conditions) concerning the attainment of the maximum saturation of the formed titanium carbide with carbon (up to 19.5 percent) at the very start of the process and its subsequent decarbonization by exposure of the product in the furnace at constant temperature.

The content of combined carbon in titanium carbide rich in carbon is lowered to about 17 percent as a result of its exposure in a mixture with coal at 1900° C in atmospheres of pure CO and H₂.

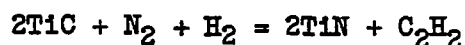
2. Analysis of the samples of titanium carbide decarbonized in an atmosphere of pure hydrogen show that the number of gram atoms of titanium exceeds the sum of gram atoms of combined carbon and the remaining oxygen. As a result of the decarbonization in an atmosphere of hydrogen, products with "empty" places in the crystal lattice of TiC are therefore obtained.

In the case of decarbonization in an atmosphere of pure CO, however, the number of gram atoms of titanium is equal to the sum of the gram atoms of combined carbon and oxygen. Thus, in the decarbonization of titanium carbide in an atmosphere of CO, a reverse interchange of part of the atoms of the carbon in the titanium carbide by oxygen occurs (process of titanium carbide oxidation by carbon monoxide).

3. The phenomena described in conclusions 1 and 2 are explained by the change in the degree of dispersity of the soot at the time of the carbonization process; the initially attained metastable saturation of the titanium carbide with carbon in the presence of soot, close to the theoretical composition of TiC, is not maintained upon exposure of the carbide in the furnace because of the decreased acting surface of the soot.

The order of the experimentally obtained difference in the composition of the metastable carbon-saturated product at the start of the carbonization change and the decarbonized product as a result of prolonged exposure is confirmed by computations that take into account the change in the free energy of the system as a result of the graphitization of the soot.

4. The presence of an admixture of nitrogen in the furnace gases (as is usually the case under production conditions) serves as an additional cause of titanium-carbide decarbonization due to the reaction



Under the practical conditions of tests made in a production furnace, the content of combined carbon in the titanium carbide during long exposure was lowered by the presence of 14 to 14.5 percent nitrogen. As analyses of such decarbonized products showed, the places in the crystal lattice that have been freed from carbon atoms are occupied by atoms of nitrogen, as a result of which single-phase products (solid solutions) of the system Ti - C - O - N are obtained.

5. The tests on titanium carbonization by heating the mixture $\text{TiO}_2 + \text{C}$ at lowered pressures confirmed the assumption that at a temperature of about 2000°C , the pure titanium carbide (TiC) at atmospheric pressure is not stable and that to obtain pure TiC under stable conditions, titanium carbonization should be conducted in a vacuum.

Translated by S. Reiss
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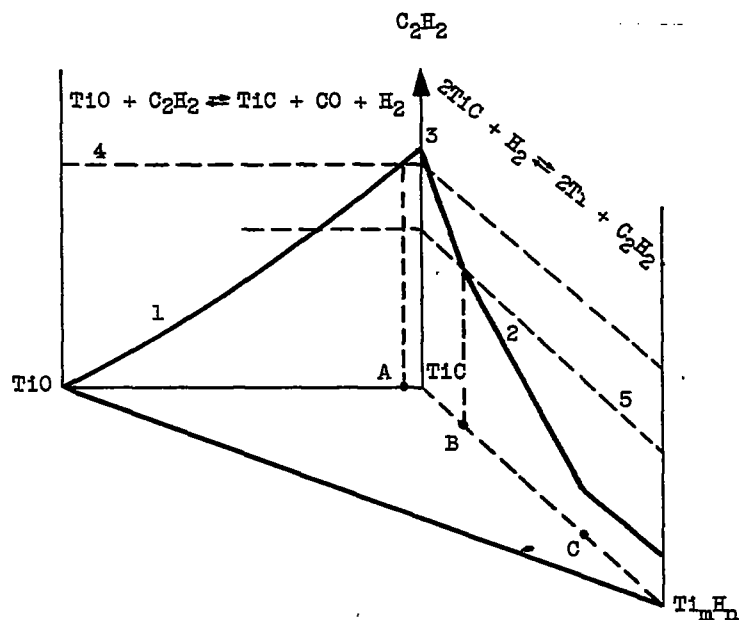
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TABLE I - CARBONIZATION AT LOWERED PRESSURES

DEPENDENCE OF COMPOSITION OF CARBONIZATION PRODUCTS ON PRESSURE AND TEMPERATURE

Pressure, mm. Hg	10				100				300				Remarks
Temperature, °C	C _{total}	C _{free}	C _{comb}	Percent C _{comb} in titanium-bearing phase	C _{total}	C _{free}	C _{comb}	Percent C _{comb} in titanium-bearing phase	C _{total}	C _{free}	C _{comb}	Percent C _{comb} in titanium-bearing phase	
1300°	19.8	12.6	7.2	8.3	29.3	29.3	0	0	30.0	30.0	0	0	*X-ray diffraction pattern does not show a NaCl type lattice. ***No nitrogen in carbonization products
	22.1	14.5	7.6	8.9	29.3	28.6	0.7	0.9*	29.5	28.1	1.4	2.0**	
1400°	20.0	7.5	12.5	13.5	19.8	9.5	10.3	11.4	18.5	11.3	7.2	8.1	
					19.1	8.3	10.8	11.8	23.9	16.6	7.3	8.8	
1500°	21.2	4.9	16.3	17.2	20.9	5.7	15.2	16.1	22.2	10.1	12.1	13.5	
	22.3	6.9	15.4	16.5	21.8	6.3	15.5	16.5	22.1	9.4	12.7	14.0	
1700°	20.6	1.6	18.0	19.3	21.5	3.5	18.0	18.7	24.6	8.9	15.7	17.2	
	21.7	3.4	18.3	18.9	21.2	4.5	17.0	17.8	19.4	3.3	16.1	16.7	
1900°	23.6	4.7	18.9	19.8	24.0	6.2	17.8	19.0	21.5	5.0	16.5	17.4	
									22.6	5.6	17.0	18.0	



- | | |
|--|---|
| <p>1 Curve of equilibrium concentration of C_2H_2 over system $TiO - TiC$</p> <p>2 Curve of equilibrium concentration of C_2H_2 over system $Ti - C$</p> <p>3 Equilibrium concentration of C_2H_2 over TiC</p> <p>4 Equilibrium concentration of C_2H_2 over soot at start of carbonization process</p> <p>5 Equilibrium concentration of C_2H_2 over graphite</p> | <p>A Composition of solid phase at instant of maximum carbon saturation at start of carbonization process ($C_{comb} = 19$ to 19.5 percent)</p> <p>B Composition of solid phase after prolonged exposure in furnace ($C_{comb} = 17$ percent)</p> <p>C Saturated solid solution of Ti in TiC ($C_{comb} \approx 7$ percent)</p> |
|--|---|

Figure 1. - Equilibrium concentration of C_2H_2 over system $TiO - TiC - Ti_mH_n$.

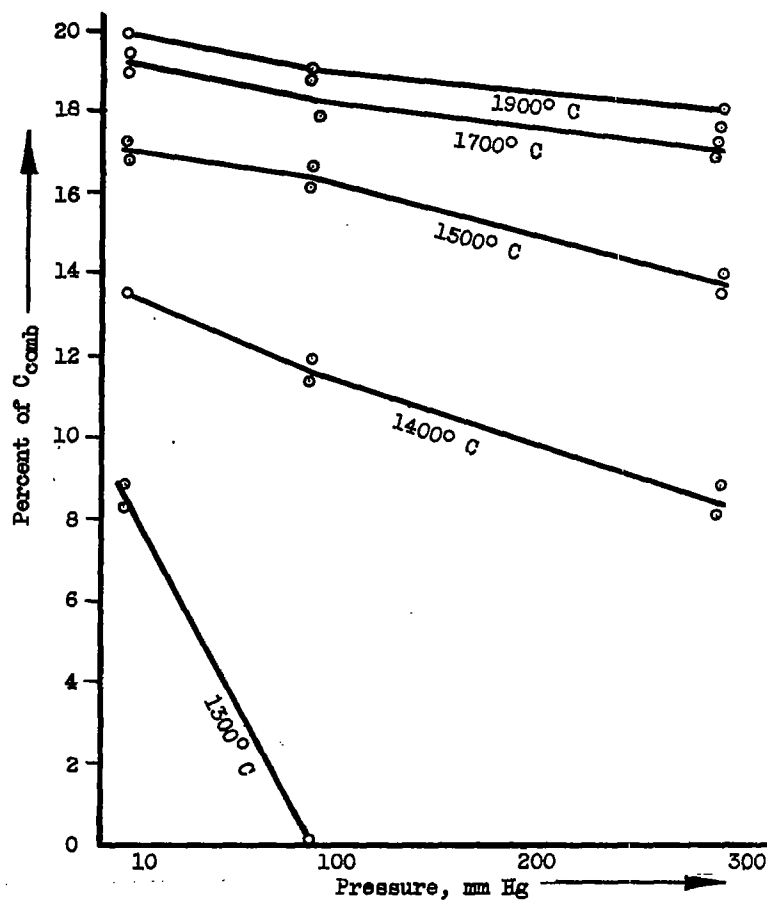


Figure 2. - Change in composition of titanium-carbonization products with pressure at various temperatures.

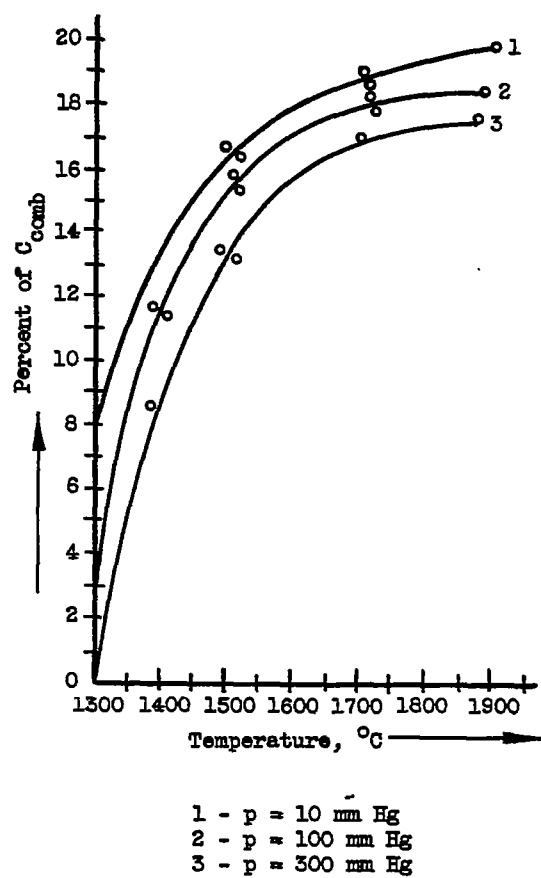


Figure 3. - Change in composition of titanium-carbonization products with temperature at various pressures.